

Appendix 7-10: Evaluation of Advanced Treatment Technologies for Mercury Effects: Chemical Treatment and Solid Separation

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INTRODUCTION

Eutrophication from excess phosphorus in Everglades Agricultural Area runoff has been acknowledged as a serious problem in the Everglades (SFWMD, 1999). The Everglades Forever Act (EFA) requires optimization of STA operations for the removal of phosphorus and other pollutants, including mercury, to protect the Everglades ecology. Currently, research in the Everglades suggests that phosphorus concentrations in discharges may need to be below 10 ppb to protect the ecology of the system (McCormick et al., 1996). In response, the South Florida Water Management District (SFWMD) has constructed artificial wetlands designated stormwater treatment areas (STAs) to lower phosphorus concentrations in agricultural runoff. However, if research and monitoring determine that the STAs cannot routinely attain the less than 10 ppb phosphorus target, then additional treatment may be required. These additional treatments are designated advanced treatment technologies (ATTs).

However, the effect of phosphorus reductions on the cycling of mercury in the Everglades ecosystem may be of concern. Existing mercury concentrations in sportfish have prompted public health authorities to issue warnings for no or limited fish consumption for the entire Everglades system. It has been speculated that mercury could bioaccumulate in Everglades biota to even higher levels as a result of the operation of the STAs and ATTs. In particular, concerns were raised about the use of periphyton-based STAs and ATTs, and chemical addition of compounds that promote mercury methylation or bioaccumulation.

The transformation of mercury into methylmercury appears to be carried out by anaerobic sulfate-reducing bacteria (Gilmour and Henry, 1991). In the Everglades and associated ecosystems, there are three areas that appear to be capable of supporting these microbes: the sediment/water interface (Gilmour et al., 1998), the extensive periphyton mats (Cleckner et al., 1999), and the root zones of floating macrophytes such as water hyacinth and water lettuce (Hurley et al., 1999). Consequently any technology that uses sediments, periphyton or floating macrophytes may potentially provide areas for

increased mercury methylation. Additionally, any technology that affects the concentration of sulfur and/or impacts the sulfate-sulfide ratio may also provide opportunities for increased mercury methylation.

The current Florida state standard for THg in surface water discharges is 12 ng/L. However, since the majority of water bodies in South Florida are in compliance but still have mercury related fish consumption advisories, the FDEP has recognized that this standard is deficient. Therefore, it is likely that this standard will be lowered. Additionally, the EFA requires “. . . a net improvement in areas already impacted.” This has been interpreted to suggest that the benefits from phosphorus reductions must be balanced against any detriments that may come from changes in other parameters, particularly increases in mercury, mercury methylation and bioaccumulation. Consequently, the District must evaluate the behavior of mercury in ATTs.

MATERIALS AND METHODS

The first ATT to be properly evaluated was a Chemical Treatment and Solid Separation (CTSS), a system that uses iron sulfate or aluminum sulfate, as well as a settling tank, to create a nutrient rich sludge. This technology was tested at two pilot plants: one upstream of STA1-W near the inflow and one downstream of the project located at the outflow. The upstream sites used iron sulfate, while the downstream site used aluminum sulfate. A generalized schematic of the technology is shown in **Figure A7-10-1**.

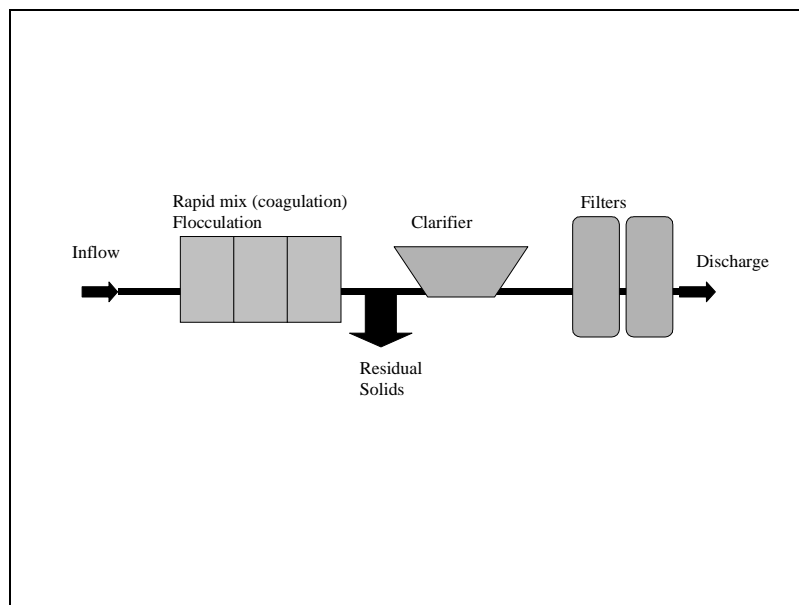


Figure A7-10-1. Generalized schematic for chemical treatment – solid separation technology.

Samples were collected on a weekly basis from the inflow, discharge and sludge following District protocols for the collection of ultra-trace total mercury (THg) and methylmercury (MeHg). The filtered and unfiltered inflow and discharge samples were analyzed for THg and MeHg. Solids residuals were approximately 1-3% solids by volume. As such the analyses were carried out as if the residuals were an unfiltered water sample and reported as ng/L rather than ng/g.

For each trip, five quality assurance samples of surface water were collected for THg and MeHg analyses: 1 Filtered Equipment Blank; 2 Filtered Field Duplicates; 2 Unfiltered Field Duplicates.

Quality assurance criteria for precision and accuracy were both set at 25%. Additional analyses for laboratory quality control were performed in the lab. The laboratory quality assurance criteria are set forth in the approved CompQAP for the contract lab.

Analytical results were examined for compliance with field quality assurance criteria. Results were also screened if they were below the detection limit (BDL) or the practical quantitation limit (PQL). Acceptable samples were then examined for significant differences. This was accomplished in two stages. First, paired inflow and outflow samples were analyzed for a 40% or greater difference. The value of 40% has previously been determined to be the upper bound of reproducibility routinely achievable for field duplicates (Rumbold, 1999). Consequently, to be considered distinct analytical results, the two samples must differ by more than 40%. Following these preliminary screenings, paired results were analyzed using a Student's t test assuming equal variances at $\alpha = 0.05$, and $\beta = 0.9$.

In addition, analytical results were compared to applicable standards for mercury concentrations in each medium.

RESULTS

Analytical results for both the upstream and downstream CTSS units are shown in **Tables A7-10-1** through **A7-10-4**. All field and laboratory quality assurance criteria were met. One datum (63.8 ng/L) collected at the upstream unit on 12/9/99 from the filtered inflow appeared to be an outlier and was excluded from any further analyses.

Inflow concentrations for THg for the upstream unit averaged 6.2 ng/L the majority of which was particulate matter (86%). Inflow MeHg averaged 0.1 ng/L, which was below the PQL. Discharge concentrations for the upstream site averaged below the detection limit for both THg and MeHg. Solids residual samples averaged 81.1 ng/L for THg. Inflow concentrations of THg at the downstream unit were less than one-fourth those at the upstream site and averaged 1.35 ng/L. Inflow concentrations for MeHg were below the detection limit. Outflow concentrations for THg and MeHg were below the PQL and MDL, respectively. Concentrations for THg in the solids residuals from the downstream unit averaged 8.0 ng/L.

Table A7-10-1. Analytical results for THg at the upstream CTSS unit using iron sulfate.

Date	Inflow (THg UF)	Outflow (THg UF)	Residual (THg UF)	Inflow (THg F)	Outflow (THg F)
12/5/99	8.7	<u>0.3</u>	189.5	<u>0.7</u>	0.3
12/9/99	8.3	0.3	40.3	<u>0.9</u>	X
12/14/99	4.1	0.3	56.9	<u>0.9</u>	<u>0.4</u>
12/20/99	4.6	0.3	55.2	Q	0.3
12/26/99	5.1	0.3	63.4	<u>1.1</u>	0.3
average	6.2	0.3	81.1	<u>0.9</u>	0.3

Table A7-10-2. Analytical results for MeHg at the upstream CTSS unit using iron sulfate.

Date	Inflow (MeHg UF)	Outflow (MeHg UF)	Sludge (MeHg UF)	Inflow (MeHg F)	Outflow (MeHg F)
12/5/99	0.159	0.049	1.935	0.049	0.049
12/9/99	0.159	0.032	0.454	0.032	X
12/14/99	<u>0.112</u>	0.050	0.797	<u>0.086</u>	0.050
12/20/99	<u>0.093</u>	0.047	0.545	0.047	0.047
12/26/99	<u>0.137</u>	0.045	0.574	0.045	0.045
average	<u>0.132</u>	0.045	0.861	<u>0.052</u>	0.048

Table A7-10-3. Analytical results for THg at the downstream CTSS unit using aluminum sulfate.

Date	Inflow (THg UF)	Outflow (THg UF)	Sludge (THg UF)	Inflow (THg F)	Outflow (THg F)
12/5/99	2.710	0.560	7.510	0.640	0.310
12/9/99	1.570	<u>0.680</u>	4.630	0.670	0.310
12/14/99	<u>0.860</u>	<u>0.330</u>	6.650	<u>0.330</u>	0.310
12/20/99	<u>0.840</u>	0.310	6.620	0.470	<u>0.610</u>
12/26/99	<u>0.780</u>	<u>0.620</u>	14.560	<u>0.780</u>	<u>0.460</u>
average	1.352	<u>0.500</u>	7.994	<u>0.578</u>	<u>0.400</u>

Table A7-10-4. Analytical results for MeHg at the downstream CTSS unit using aluminum sulfate.

Date	Inflow (MeHg F)	Outflow (MeHg F)	Inflow (MeHg UF)	Outflow (MeHg UF)	Sludge (MeHg UF)
12/5/99	0.049	0.049	0.049	0.049	0.049
12/9/99	0.032	0.032	0.032	0.032	<u>0.046</u>
12/14/99	0.050	0.050	0.050	0.050	<u>0.050</u>
12/20/99	0.047	0.047	0.047	0.047	<u>0.083</u>
12/26/99	0.045	0.045	0.045	0.045	0.339
average	0.045	0.045	0.045	0.045	0.113

Legend for Tables

All units in ng/L

Bold values indicate result below detection limit

Underlined values indicate result below the practical quantitation limit

X indicates sample destroyed in shipping

Q: filtered inflow results from 12/20 are 63.8 ng/L and appear to be an outlier.

Given that for both units the average THg outflow was below the PQL (and in the case of the northern unit BDL), it is unnecessary to carry out any statistical analyses to determine whether or not the outflow was different from the inflow. Indeed the upstream and downstream units removed more than 95% and 67% of the THg, respectively. Since the majority of the MeHg data was BDL, a similar analysis cannot be carried out on the outflow data.

Using hydrologic data from the primary contractor, it is estimated that 95% of the water entering the system exited through the outflow and that 5% of the water was routed to the solids residuals. Given these values, a simple mass budget can be calculated. Using the average values, the upstream site residuals and outflow account for 70% of the THg and 65% of the MeHg estimated in the inflow waters. Similarly, the downstream residuals and outflow account for 65% of the THg and 108% of the MeHg estimated in the inflow waters.

Additionally, the primary contractor has reported total suspended solids (TSS) data for the solids residuals. Using this data it is possible to estimate the concentrations of THg in the dewatered residuals. At the upstream site the TSS in the residuals was 1500 mg/L. Given an average THg concentration of 81.1 ng/L this would create a solid with a THg concentration of 54 ng/g. Similarly, the TSS at the downstream site was 2000 mg/L. Given an average THg concentration of 8.0 ng/L, this would create a solid with a THg concentration of 4 ng/g.

DISCUSSION

The CTSS technology did not appear to elevate MeHg concentrations in the discharge. Additionally, based on the crude mass balance, the technology did not appear to transform THg into MeHg in the residuals. As such, the technology appears not to increase mercury methylation rates. Additionally, concentrations of mercury species in the dewatered sludge do not violate any State or Federal criteria. In fact, the northern site residual samples are similar to concentrations found in peat soils in the Everglades Agricultural Area. In contrast, southern site residual samples have concentrations of mercury similar to those in aquatic plants.

Further investigation on solids residual disposal, particularly in chemical treatment and managed wetlands technologies, is currently being evaluated by the SFWMD as part of the ATT program.

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